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Tito E. Huber

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14. ABSTRACT
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Report Title

Electronic Transport Control of Bismuth Nanowires

ABSTRACT

Theoretical models of the effect of quantum confinement in nanowire arrays show that thermoelectric cooler efficiency can be enhanced several-fold using this strategy. Previous experimental studies of well characterized samples failed to show an enhancement of the thermopower, but the reason for this failure was not identified. We show that bismuth nanowires have, in addition to bulk electrons and holes, a third type of charge carriers (surface charges). The effect of surface charges is to shift the range of diameters over which the relevant phenomena occurs. We investigated the range of diameters 20-200 nm and report thermopower enhancements in 35 nm Bi nanowire arrays. We also show that array's thermoelectric properties can be further optimized by applying a magnetic field.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1.“Constitutional Supercooling and the growth of 200-nm Bi-Sb wire array composites”.
T.E. Huber, O Anakoya, and M.H. Ervin
Journal of Applied Physics 92, 1337 (2002).

2. “ Electronic Transport in a 3-D Network of 1-D Bi Quantum Wires”
M.J. Graf and T.E. Huber
Physica E18, 260 (2003).

3.“Longitudinal Magnetoresistance of Bi Nanowires”
T.E. Huber and M.J. Graf
Physica E18 223 (2003).

5. Shubnikov-de Haas Oscillations in the Contact Resistance of Bi Nanowires,
T.E. Huber, A. Nikolaeva, D. Gitsu, L. Konopko, M.J. Graf, and C.A. Foss, Jr.
Mat. Sci. and Eng. C. 23 1099 (2003).

6.“Longitudinal magnetoresistance in single crystal wires of pure and doped bismuth in wide range of diameters”
D. Gitsu, T. Huber, L. Konopko, and A. Nikolaeva.
Phys. Stat. Sol. (a) 196, 137 (2003).

7.Magnetoquantum oscillations and confinement effects in arrays of 270-nm-diameter bismuth nanowires.
T.E. Huber, K. Celestine and M.J. Graf,
Phys. Rev. B67 245317 (2003).

8. “Magnetic Anisotropy and de Haas–van Alphen Oscillations in a Bi Microwire Array Studied via Cantilever Magnetometry at Low Temperatures,”
M.J. Graf, C.P Opeil, and T.E. Huber.
J. Low Temp. Physics 134, 1055 (2004).

9.Confinement Effects and Surface Charge in Bi Nanowires
T.E. Huber, A. Nikolaeva, D. Gitsu, L. Konopko, C.A. Foss, Jr., and M.J. Graf.
Appl. Phys. Let 84, 1326 (2004).

10.Thermoelectric properties of quantum Bi wire doped with Sn at electron topological transitions induced by stretch and doping.
A. Nikolaeva, D.V. Gitsu, T.E. Huber, L. A. Konopko, P.P. Bodiul, Gh. Para.
Reviews on Advanced Materials Science, 8, 34 (2004).

11.Conductivity in quantum wires in a homogeneous magnetic field
E.P. Sinjavsky, R.A. Khamidullin, T.E. Huber, A.A. Nikolaeva and L.A. Konopko.
Reviews on Advanced Materials Science. 8, N2, 34-40, (2004).

12.MagnetoSeebeck Coefficient of a Bismuth Microwire Array in a Magnetic Field Y. Hasegawa, Y. Ishikawa, H. Morita, T. Komine, T.E. Huber, A. Sizuki, and H. Shirai,
Appl. Phys. Lett. 85, 917 (2005).

13.“Pressure dependent thermopower of individual Bi nanowires.”
D. Gitsu, L. Konopko, A. Nikolaeva and T.E Huber.Appl. Phys. Lett. 86, 102105 (2005).

14.Quantum Confinement and Surface State Effects in Bismuth Nanowires Tito E. Huber, A. Nikolaeva, D. Gitsu, L. Konopko, and M.J. Graf. Physica E37, 194 (2006).

Number of Papers published in peer-reviewed journals: 14.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Quantum Interference of Surface States in Bismuth Nanowires probed by the Aharonov-Bohm Oscillation of the Magnetoresistance. A. Nikolaeva, D. Gitsu, L. Konopko, M.J. Graf and T.E. Huber.http://arxiv.org/ftp/cond-mat/papers/0702/0702368.pdf.

Number of Papers published in non peer-reviewed journals: 1.00

(c) Presentations

I)Invited Talk Title: Thermoelectric Properties of Bi Nanowires
XIII International Materials Research Congress
International materials Research Society
Cancun, Mexico
August 23, 2004

II) Talk Title: Bi(2)Te(3) Nanothermocouple based Single-Photon Mid-infrared Detector.
May 31, 2005
Army Research Office
Invited by Alma Wickenden and Matt Ervin. This shows that there were significant interactions of the PI with the Army Research Laboratory.

III)Talk Title: Quantum Confinement Effects and Surface-Induced Charge Carriers in Bi Quantum Wires
March Meeting APS 2006.

IV)Invited Talk Title: Thermoelectric Properties of Bismuth Nanowire Composites
2006 Direct Thermal energy Conversion Workshop
Aug 29-Sep 1, 2006

V) Colloquium Title: Nanomaterials for Direct Thermal to Electric Conversion
Place: Department of Physics Colloquium
Saint Johns University, Queens, NY
Date: April 11, 2007

VI) Invited Talk Title ¨Thermoelectric Properties of Bi Nanowire Array Composites¨
Place: 2007 International Forum on Thermoelectricity, Chernovsti, Ukraine.
Date: July 16, 2007

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Peer-Reviewed Conference Proceeding publications (other than abstracts):

1)Thickness Dependence of the Thermoelectric Properties of Sn-doped Single Crystal Bi-Wires
D. Gitsu, T. Huber, L. Konopko, A. Nikolaeva.
Proceedings of the International Conference on Thermoelectrics held in Grande-Motte, France. Published by IEEE, USA (2003)

2)Thermoelectric Power of a Network of 6-nm Bi Nanowires in a Porous Vycor Glass Matrix
T.E. Huber, K. Celestine, A. Nikolaeva, A. Gitsu, D. Konopko, J. Huang, and M.J. Graf.
Proceedings of the International Conference on Thermoelectrics held in Grande-Motte, France. Published by IEEE, USA (2003)

3) Title: Thermoelectric Properties of Small Diameter Bi Nanowires: Evidence for Surface Charge
T.E. Huber, A.A. Nikolaeva, D.V. Gitsu, L.A. Konopko, and M.J. Graf.
Proceedings of the International Conference on Thermoelectrics held in Vienna, Austria. Published by IEEE, USA (2006)

4) Title: Thermoelectric power of Sinlge Bi Microwires at helium Temperatures
D.V. Gitsu, T.E. Huber, L. Konopko and A.A. Nikolaeva.
Proceedings of the International Conference on Thermoelectrics held in Vienna, Austria. Published by IEEE, USA (2006).

5) Title: Electrical Contact Resistance of Bismuth Telluride Nanowires
P.Jones, J. Melngailis, J. Barry, T.S. Zeleva, A. Nikolaeva, L. Konopko, and M. J. Graf.
Proceedings of the International Conference on Thermoelectrics held in Vienna, Austria. Published by IEEE, USA (2006).

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 5

(d) Manuscripts

A. Nikolaeva, D. Gitsu, L. Konopko, M.J. Graf and T.E. Huber.
Quantum Interference of Surface States in Bismuth Nanowires probed by the Aharonov-Bohm Oscillation of the Magnetoresistance.
http://arxiv.org/ftp/cond-mat/papers/0702/0702368.pdf.
Submitted to Physical Review in March 2007.

A. Nikolaeva, L. Konopko and T.E. Huber
Diameter-dependent Thermopower of Bismuth Nanowires
Submitted to Physical Review in July 2007

Number of Manuscripts: 2.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
O. Aluko	0.00
FTE Equivalent:	**0.00**
Total Number:	**1**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Tito E. Huber	0.30	No
FTE Equivalent:	**0.30**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
Paetrice Jones	0.01
Kizi Celestine	0.01
Tosin Adunfa	0.00
Ajibola Abekele	0.00
FTE Equivalent:	**0.02**
Total Number:	**4**

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 2.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 2.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 2.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 2.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

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FTE Equivalent:	
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Attachment to the Final Report of the project entitled

"Electronic Transport control of Bismuth Nanowires". Funding Numbers 43807-MS

FOREWORD

Theoretical models of the effect of quantum confinement in nanowire arrays show that thermoelectric cooler efficiency can be enhanced several-fold using this strategy. Previous experimental studies of well characterized samples failed to show an enhancement of the thermopower, but the reason for this failure was not identified. We show that bismuth nanowires have, in addition to bulk electrons and holes, a third type of charge carriers (surface charges). The effect of surface charges is to shift the range of diameters over which the relevant phenomena occurs. We investigated the range of diameters 20-200 nm and report thermopower enhancements in 35 nm Bi nanowire arrays. We also show that array's thermoelectric properties can be further optimized by applying a magnetic field.

Author: Tito E. Huber,
Howard University
500 College St. N.W., Washington, DC 20059
(202)806-6768 thuber@howard.edu, edtech01@erols.com

Title: Final Report of Electronic Transport Control of Bismuth Nanowires. 43807 MS"

TABLE OF CONTENTS

I. STATEMENT OF THE PROBLEM STUDIED.

Our project aims to impact the technology of solid state thermoelectric coolers for night vision devices. Solid-state cooling technology can be employed in high performance applications if the thermoelectric conversion efficiency of the materials is increased by factor-two from the current value. In our project, the approach to achieve this level of improvement involve the electronic transport in materials consisting of dense arrays of bismuth nanowires. Theoretical models of the effect of quantum confinement in Bi nanowire arrays, by Hicks and Dresselhaus [1], show that the thermoelectric efficiency can be raised to the required level using this strategy.

Bulk Bi is a semi-metal that is a low temperature thermoelectric because of its high electronic mobility, its low Fermi energy, and low thermal conductivity. In a Bi nanowire, the effect of lateral confinement is to raise the zero-point energy of electrons and to lower that of the holes by the confinement energy $\pi^2 h^2 / m^* d^2$, where h is Planck's constant and m^* is the corresponding carrier in-plane effective mass transverse to the wire axis. Quantum confinement can decrease the band overlap to the point that, for very fine wires, the semimetal can transform into a semiconductor. The detailed model of quantum confinement-induced semimetal-to-semiconductor (SMSC) transition in Bi nanowires [1], predicts that the SMSC transition occurs at $d \sim 55$ nm (for wires that are oriented along the trigonal direction). The argument for improved thermoelectric properties assumes that confinement packs the carriers into one-dimensional subbands in the gap. Let us assume that a given subband, consisting of states that differ in the quasiparticle momentum parallel to the wire length, starts at E. Furthermore we assume that the electronic system is prepared so that the Fermi level, E_F, is tuned to correspond to the energy E. Because the density of states (DOS) is singular ($DOS \sim (E_F\text{-}E)^{-1/2}$) for such system, the resistance is low and the thermopower that is the logarithmic derivative of the DOS, is enhanced. In the past decade, there have been many projects, some under Army and DARPA sponsorship, that aimed at demonstrating this effect. However, these previous studies have failed to conclusively demonstrate thermopower enhancements. In the first stage of the project, we report identifying the reason for this failure. We will show that the reason is that bismuth nanowires have, in addition to bulk electrons and holes, a third type of charge carriers (surface charges). In the second stage of the project, we report thermopower enhancements in 35 nm Bi nanowire arrays and magnetic field effects that we will argue are due to quantum confinement.

Angle-resolved photoemission spectroscopy (ARPES) studies of Bi surfaces have shown that Bi nanowires support surface states, with high carrier densities of around $5\times 10^{12}\,cm^{-2}$ and large effective mass [2]. Our own studies of the transport properties (using the Shubnikov-de Haas (SdH) method) of 30-nm diameter Bi nanowires support the model of surface charges [3]. These carriers are located on the surface of the nanowire and have higher effective masses than that of the bulk electrons and holes. Therefore the range of diameter over which the SMSC transition occurs is moved to smaller diameters. The range of diameters that has to be investigated is not, as in previous studies, the 40+ nm range but the 20+ nm range. Furthermore, according to our estimates, the thermopower of this two dimensional sheet of charge should dominate the thermoelectric properties. This is a good start because the surface states are by construction restricted to the periphery of the nanowire and restricted from the core of the nanowire.

We base our research in previous studies of the electronic transport properties of the wire array samples. A review of these studies follows. We employ the high pressure injection [3] method to prepare arrays of nanowires. When the injection pressure is adjusted to be very high, the injection is full (all the channels of the template are full with bismuth) and the orientation trigonal axis //wirelength, is illustrated in Fig. 1.

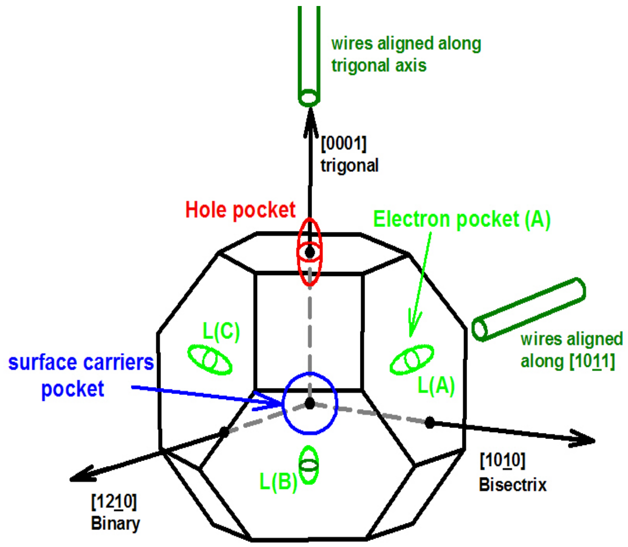


Figure 1. *Fermi Surface of bulk Bi, showing the Brillouin zone with the fifth-band hole pocket about the T-point and the three sixth-band L-point electron pockets labelled A, B, and C. The crystalline orientation of two types of wires that can be grown is shown. High pressure injection yields nanowires having their wire axis along the trigonal axis or trigonal wires, the three electron pockets are crystallographically equivalent. The pocket labeled surface carriers will be discussed below. We also show the orientation of nanowires grown by M. Dresselhaus at MIT, oriented along [1011]. There nanowires have the binary symmetry. We have access to nanowires with this orientation through a collaboration. These nanowires are grown by direct casting of microcapillaries [4].*

This project required a method for analyzing the charge carriers involved in electronic transport. We made use of the Shubnikov-de Haas method [5] that can be employed to measure the charge density, that is the volume, and anisotropy of the Fermi surface (FS) and carriers effective masses. A precondition for applying this method is the ability to prepare samples of very high mobilities. Reference 3 only discusses the case of 30-nm wires but, recently, we have applied this method to a number of samples of large diameters that also exhibit SdH oscillations. Reference 6 shows results for 50 nm nanowires. The main results are shown in Figure 1 and Figure 2. We observe two types of carriers, that is two Fermi surfaces. One type of carriers correspond to the bulk carriers of low effective mass that are size quantized as the nanowire diameter gets smaller (red ellipsoids in Fig 1). In trigonal wires the bulk states that we observe are holes. The other type of carriers are surface modes (blue) that have high effective mass. The identification of bulk versus surface modes is done on the basis of anisotropy and effective mass. In Fig. 1, the diameter of the sphere that represents the surface carriers is dependent upon the diameter of the nanowires because the volume of the sphere is the carrier concentration. For example, in the case of 50 nm wires, the ratio of the bulk carriers concentration to that of surface carriers is found to be ~1/6. The experimental results are shown in Figure 2. The full analysis of the Fermi surfaces supports the picture presented in Fig. 2. For example, the anisotropy of the Fermi surface of "bulk carriers" (not shown) change from being very asymmetric for the bulk(1/d=0) to being spherical symmetric near the SMSC transition. Instead, the FS obtained from the short period is spherically symmetric.[3]

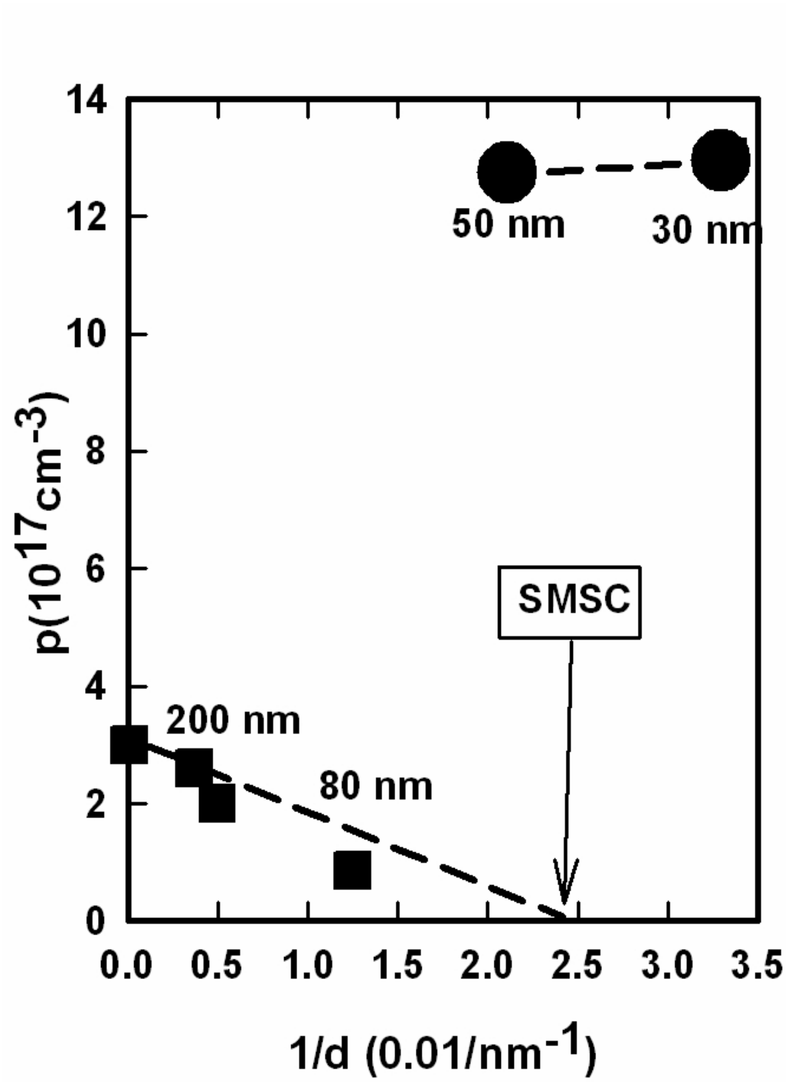


Figure 2. *Hole density for bulk Bi (1/d=0) and for Bi nanowires of various diameters at low temperatures using the Shubnikov-de Haas method. We observe two Fermi surfaces and therefore two periods, a short and a long one. The data for the long period FS is indicated with squares and is believed to be represent bulk carriers. The data for the short period is shown as full circles and is interpreted as surface charges. The dashed lines are an aid to the eye. The dashed line in the bottom of the figure shows the expected results for a SMSC transition with a critical diameter of 55 nm.*

Figure 3 shows the surface states as a sheath of charges in the nanowires. The presence of surface states in the nanowires can transform them into nanotubes. As we shown in Section VI there are strong indications that this in indeed the case because the nanowires exhibit Aharonov-Bohm oscillations that are generally observed in tubes or rings.

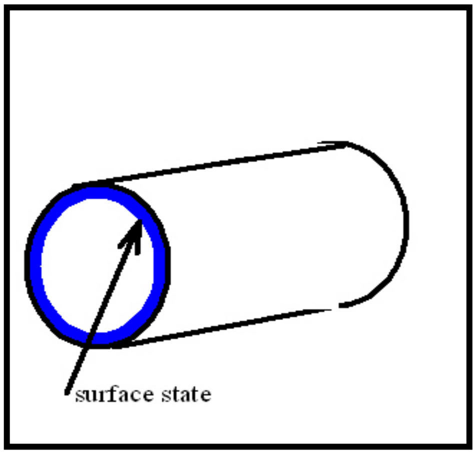


Figure 3. *Representation of the surface states. The penetration length of the surface state in the core of the nanowire is believed to be tens of nanometers in the case of trigonal wires. This is found by estimating the diameter of the orbits of carriers in real space that give the SdH oscillation.*

SECTION II. THEORY. THERMOPOWER OF NANOWIRES WITH SURFACE CHARGES.

The thermopower of Bi nanowires with surface charges can be estimated as follows. Assuming a two-dimensional (2D) model and a parabolic dispersion relation, the number of states per unit area (NOS), considering spin, is

$$NOS = m_0 m^* E_F / \pi\hbar^2 \tag{1}$$

where m_0 is the free electron mass, m^* is the effective mass, and E_F is the Fermi energy. The number of states (*NOS*) equals the number of surface carriers per unit area Σ which is the parameter that is measured in ARPES [2] and SdH [3] experiments. According to ARPES, $\Sigma \sim 5\times10^{12}\,cm^{-2}$. In the SdH of 30 nm Bi nanowire arrays, [3] it was observed that $\Sigma \sim 2\times10^{12}\,cm^{-2}$. Therefore, taking $m^* = 0.3$ [2,3], and the SdH value of the number of surface carriers per unit area, we find that E_F =39 meV.

Assuming standard diffusive conditions (the phonons are thermalized), the thermopower of the surface carriers is given by (see Ref. [6] for a discussion):

$$S_S = (k_B^2 \pi^2 T / 3e)(1 + s/E_F) \tag{2}$$

where the energy dependence of the mobility is E^s. In the case that the mobility is limited by boundary scattering, one takes s=0.

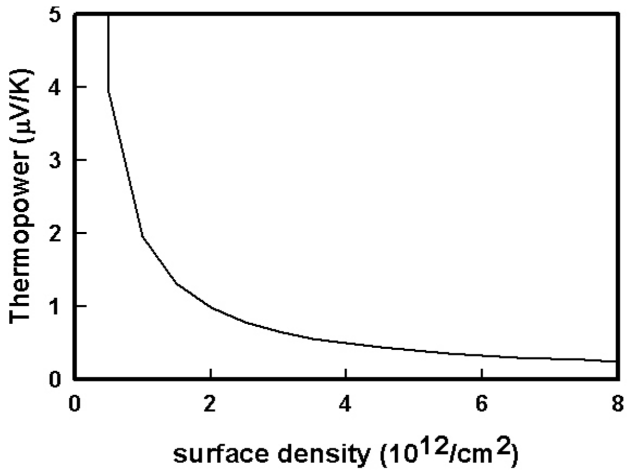


Figure 4. *Thermopower of surface states from Eq. 1 and 2.*

Figure 4 shows the absolute value of the thermopower calculated using Eqs. 1 and 2. Notice that the sign of the partial thermopower is related unambiguously to the sign of the charge of the carriers. Also note that the thermopower is dependent upon the value of the surface charge and, is independent of the wire diameter.

The total thermopower S of the Bi nanowires, assuming diffusive thermopower, is the weighted average of the partial thermopower of the carriers involved (bulk and surface carriers):

$$S = \frac{N\mu_S S_S + n\mu_E S_E + p\mu_H S_H}{N\mu_S + n\mu_E + p\mu_H} \qquad (3)$$

Here S_s is the partial thermopower of surface carriers. S_E is the partial thermopower of "bulk like"electrons and S_H is the partial thermopower of "bulk like"holes. T is the absolute temperature in Kelvin. In bulk Bi S_E~-1 T μV/K^2 and S_H~+3 T μV/K^2. We assume the S_E and S_H of Bi nanowires do not deviate very far from the values for the bulk. μ_E and μ_H are the mobilities of (bulk-like) electrons and holes in the nanowires and these parameters are dependent upon wire diameter. N is the number of surface carriers per unit volume. Note that $\Sigma = 1.8\times10^{12}\,cm^{-2}$ corresponds to a volumetric density N of $1.8\times10^{12}\,cm^{-2}\times Area.nanowire/Volume.nanowire = 1.8\times10^{12}\,cm^{-2}\times(d/2)/(\pi d^2/4)$, that is diameter dependent. For example for d=30 nm, we find N=$1.3\times10^{18}\,cm^{-3}$ In comparison the number of electrons n and holes p per unit volume in bulk Bi are n= p=$1.3\times10^{18}\,cm^{-3}$ at room temperature. At low temperatures, and in bulk Bi, $n= p=1.3\times10^{17}\,cm^{-3}$. In nanowires, the densities of electrons and holes are denoted as n and p, respectively. As shown in Fig. 2, n and p are also diameter dependent and also, it can be expected that they are strongly temperature dependent (even more so than in bulk Bi) because of the gap that develops due to the SMSC transition.

Table I. Overall, our interpretation is that there are three carriers in Bi nanowires. The main properties that characterize these carriers are the following.

		Surface carriers	Bulk-like electrons	Bulk –like holes
Charge (Unit charge Electron))		-1	-1	+1
Effective mass (Unit mass electron)		0.3 from ARPES [2] and SdH [3].	0.02	0.02
Density	d=60 nm	$N=1.3\times10^{18}\,cm^{-3}$	$n=3\times10^{17}\,cm^{-3}$ @T=0K $3\times10^{18}\,cm^{-3}$ @T=100K	p=n
	d=30 nm	$N=2.6\times10^{18}\,cm^{-3}$		
	d=20 *nm*	$N=4\times10^{18}\,cm^{-3}$		

SECTION III. SAMPLE PREPARATION AND THERMOPOWER MEASUREMENTS

Figure 5 illustrates the schematic experimental setup for the thermopower measurements.

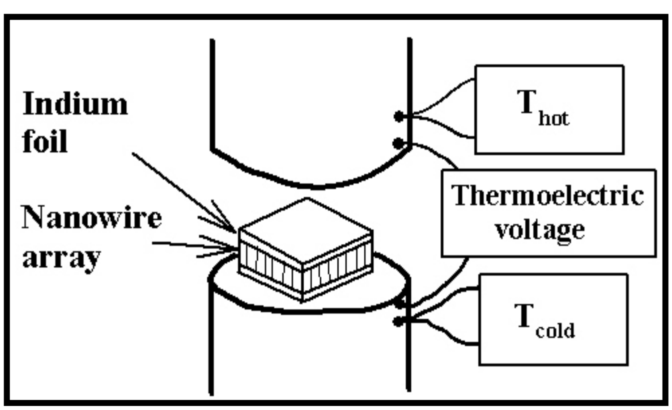


Figure 5. *Sketch of the equipment used for the thermopower measurements. The arrangement is that of an anvil. The indium foil was used to make electrical and thermal contact and to avoid breaking the array when the anvil jaws apply pressure.*

Figure 6 presents our experimental data of 200-nm and 60-nm nanowires, as well as data from Reference 7. The 200-nm nanowires are synthesized from Anopore templates. The 60- nm nanowires were prepared using templates that become available through a collaboration with Wei Yand, of Tianjin U, China. We also employed templates that were purchased to Synkera Technologies, Longmont, CO. Figure 6 presents our most recent data for Bi nanowires in the 60+ nm range..

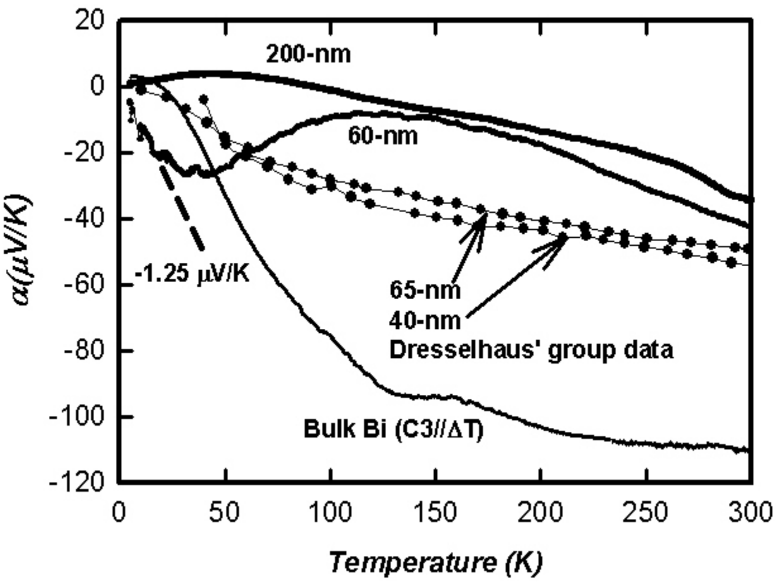
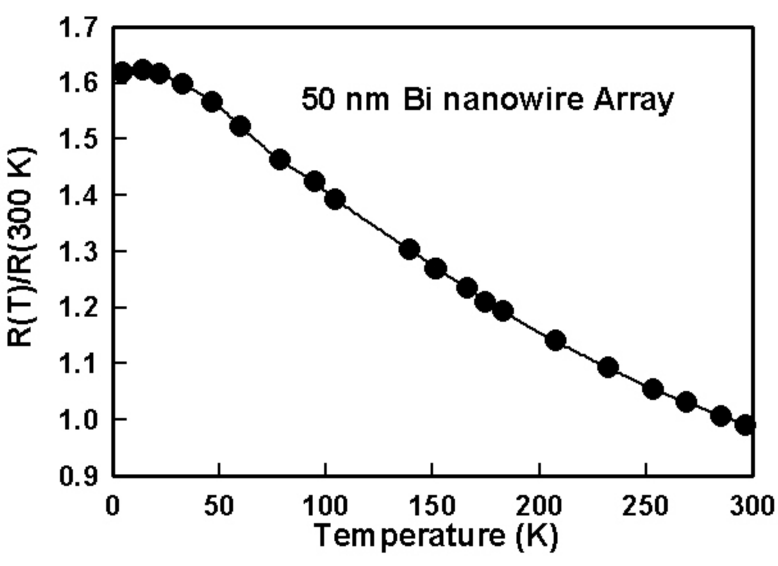


Figure 6. Top. *Thermopower of arrays of Bi nanowires of various diameters and sources. The 200-nm and 60-nm data is ours. The 200 nm diameter templates are Anopore. The 60 nm templates are from Wei Yang, Tianjin U. .The data from publications and reports to Darpa by the Dresselhaus-group is clearly indicated.*



Bottom part of Fig. 6 (See previous figure). *Resistance of the 60-nm Bi nanowire array samples.*

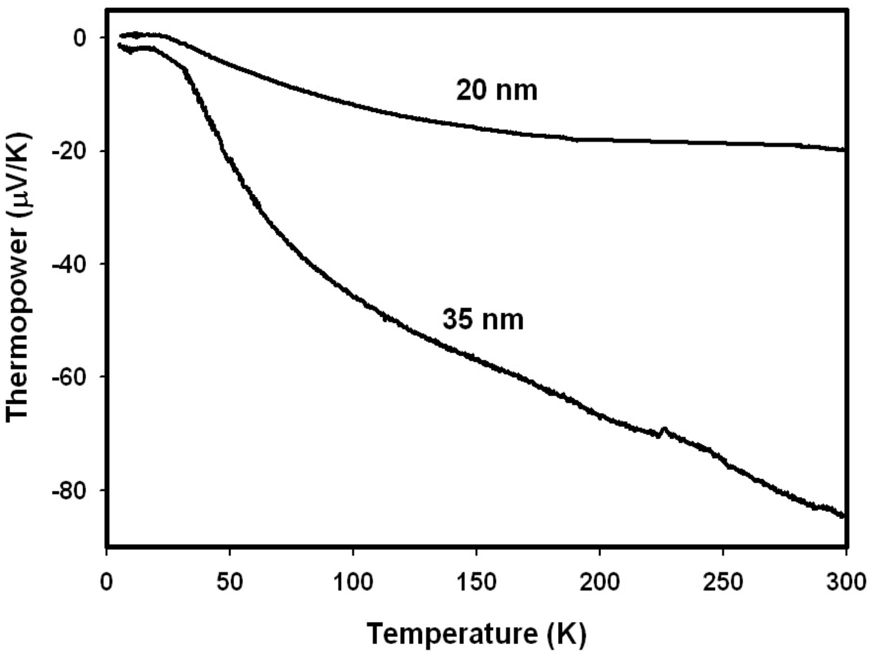


Figure 7. *Thermopower of the 20-nm and 35-nm Bi nanowire array samples. The templates a sold by Synkera Technologies.*

Our interpretation of the data in Fig. 6 and 7 is as follows. The data for <u>200-nm nanowires</u> can be interpreted in terms of Eq. 3 by neglecting the surface term, as shown in Ref. 4. We assume and it is accepted generally that, in 200-nm Bi nanowires, *n* and *p* are the same as in the bulk. At high temperatures (T > 50 K), the mobility of electrons and holes is limited by bulk mechanisms (phonon scattering) and then $\mu_E \sim 10\ \mu_H$; then, the thermopower is dominated by electrons, the thermopower is negative and similar to that of bulk Bi. We present supporting data in Section IV. The thermopower of 200-nm Bi nanowire arrays is positive at low temperatures because boundary scattering is more effective for electrons than for holes. In other words at low temperatures $\mu_E \sim \mu_H$. This is reasonable because electrons, having smaller effective masses than holes, are more easily scattered than holes by the nanowire surface. The <u>60-nm</u> nanowires thermopower data evidences a mixed electronic transport behavior as demonstrated by the complex behaviour of the thermopower. As shown in Fig. 2, at low temperatures, the density of "bulk-like" carriers is very small. Therefore, the linear negative thermopower is interpreted in terms of surface charges. From S_E=-1.25 T μV/K (Fig. 6), and from the theory results in Fig 4, we find a surface density *N* of $2.0\times10^{12}\,cm^{-2}$ in fair agreement with ARPES [2] and SdH [3].

The 60-nm diameter data shows, with a maximum at 130 K, a bump similar that to that exhibited by the 200-nm data. We interpret this bump as evidence of the presence of "bulk-like" carriers at high temperatures. This is surprising at first sight because Fig. 2 show that the "bulk-like" carrier density is close to zero for wires in this diameter range; however, the data for Fig 2 was gathered at low temperatures. If there is a gap in the 60-nm nanowires in the present study, it is very shallow; at high temperatures we can expect a substantial population of "bulk-like" carriers as it is observed. Therefore, as anticipated, the high temperature data in Fig. 6 bears evidence of the three carriers (surface at low temperature and bulk-like at high temperatures). Another interesting aspect of this data is that the linear thermopower due to surface states appears to be important even at 50 K (the surface states survive at high temperatures). In retrospect, this is not surprising because ARPES observations are performed at 130 K.

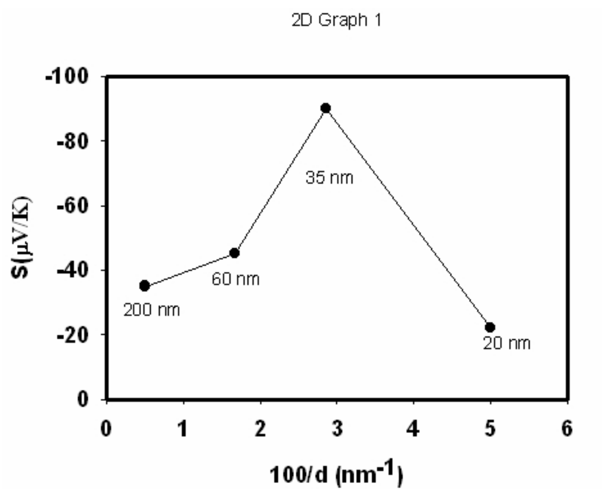


Figure 8. *Room temperature thermopower of the Bi nanowire array samples as a function of inverse wire diameter.*

In the remaining of the present section we discuss the results for small diameter nanowires that is presented in Fig. 7. The thermopower of 35-nm nanowires is much larger than that of 60-nm and 20-nm Bi nanowires and this is the remarkable size effect that we are presenting. In fact the strength of the thermopower of 35-nm nanowires rivals that of Bi single crystals. The experimental result presented in Fig. 8 can be understood as a quantum confinement effect where a subband of low carrier density (the thermopower is inversely proportional to the carrier density) is at the Fermi level in 35-nm diameter Bi wires We believe that this result can be optimized (by tuning the wire diameter, for example).

SECTION IV. THERMOPOWER OF LARGE DIAMETER Bi NANOWIRES

In order to make sure that we understood large diameter nanowires and the mechanism of limitation of the mobility in this simple case, we studied of electronic transport in individual Bi nanowires of large diameter relative to the Fermi wavelength. Measurements of the thermopower (and resistance) of intrinsic and Sn-doped Bi wires with various wire diameters, ranging from 150-480 nm, were carried out over a wide range of temperatures (4-300 K) and magnetic fields (0-14 T). These results are presented in Fig. 9

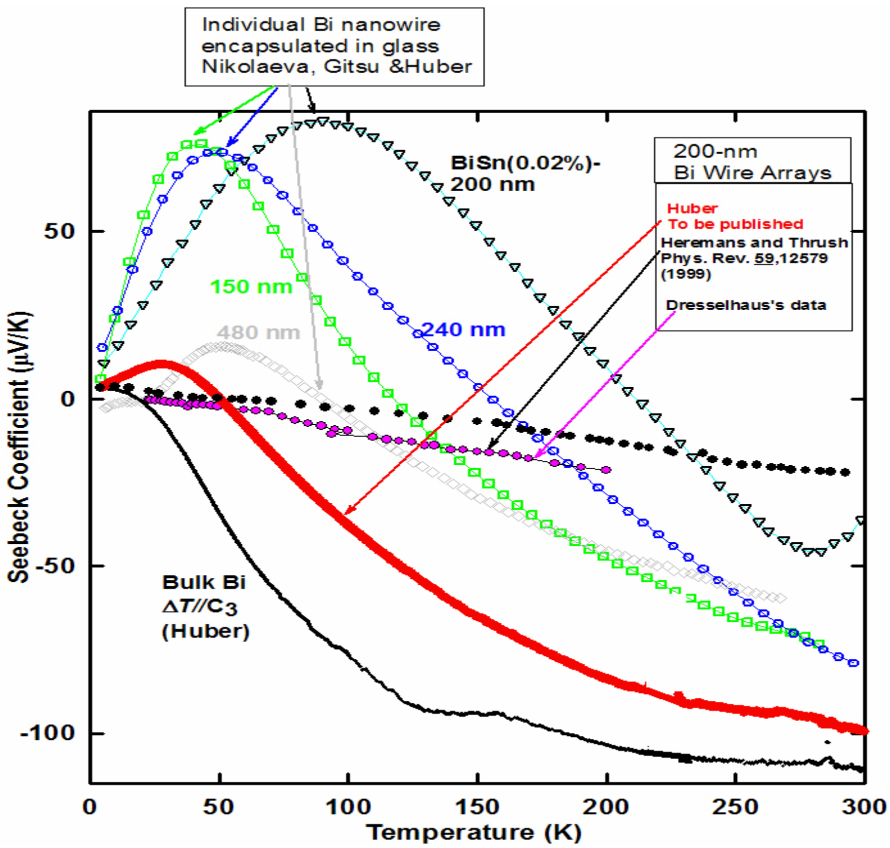


Figure 8. *Thermopower of the large diameter Bi nanowire samples investigated in the project.*

The thermopower of intrinsic Bi wires in this diameter range is positive (type-p) below about 150 K, displaying a peak at around 40 K. In comparison, intrinsic bulk Bi is type-n. Magneto-thermopower effects due to the decrease of surface scattering when the cyclotron diameter is less than the wire diameter were measured also. The measurements were interpreted in terms of a model of diffusive thermopower, where the mobility limitations posed by hole-boundary scattering are much less severe than those due to electron-hole scattering. This work, that is a collaboration with A. Nikolaeva of the Academy of Sciences of Moldova, has been submitted to Physical Review under the title "Diameter-dependent thermopower of bismuth nanowires".

SECTION V: <u>DOPING EXPERIMENTS.</u>

We tried the approach of removing surface states in our nanowires. Our idea was to counter-dope the surface carriers, that are electron-like according to our thermopower measurements, with an electron-acceptor impurity, Sn. This would have had the effect of decreasing the NOS in Eq. 1, decreasing E_F in Eq. 2, therefore INCREASING the contribution of the surface states to the thermopower *S*. This does NOT work as we show below.

Figure 9 shows the concentration of bulk carriers in bulk $Bi_{1-x}Sn_x$ from the literature.

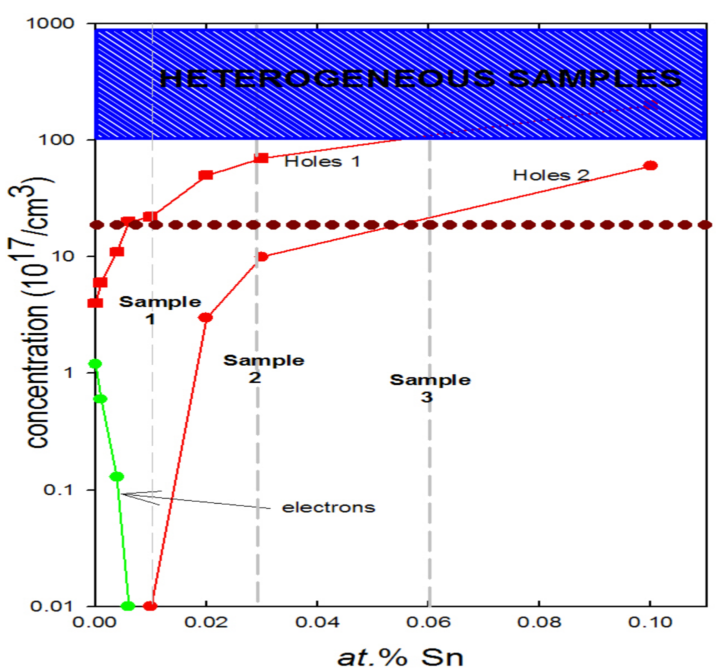


Figure 10. *Concentration of electrons and holes in bulk Bi according to Tanaka (Ref.8.). The grey vertical lines represent samples available to our effort (28/08/2006). These samples have at. % concentrations of 0.01, 0.026 and 0.06. The blue horizontal box represent bulk samples of concentrations that have been found to have occlusions of Sn (the alloy is not homogeneous; see Elzinga and Uher (Ref. 9) and also Heremans (Ref. 10)).The horizontal line represents the volumetric concentration of surface carriers (4σ/D).*

First of all it is important to notice that we use templates from Synkera whereas in the results presented in Figure 6 we used templates made by Wei Wang.. Synkera templates are sturdier, thicker and available commercially. As a note, examination of these results show that the slope of the thermopower at low temperatures is smaller than for Yang's templates indicating higher density of surface carriers. The results are shown in Figure 11.

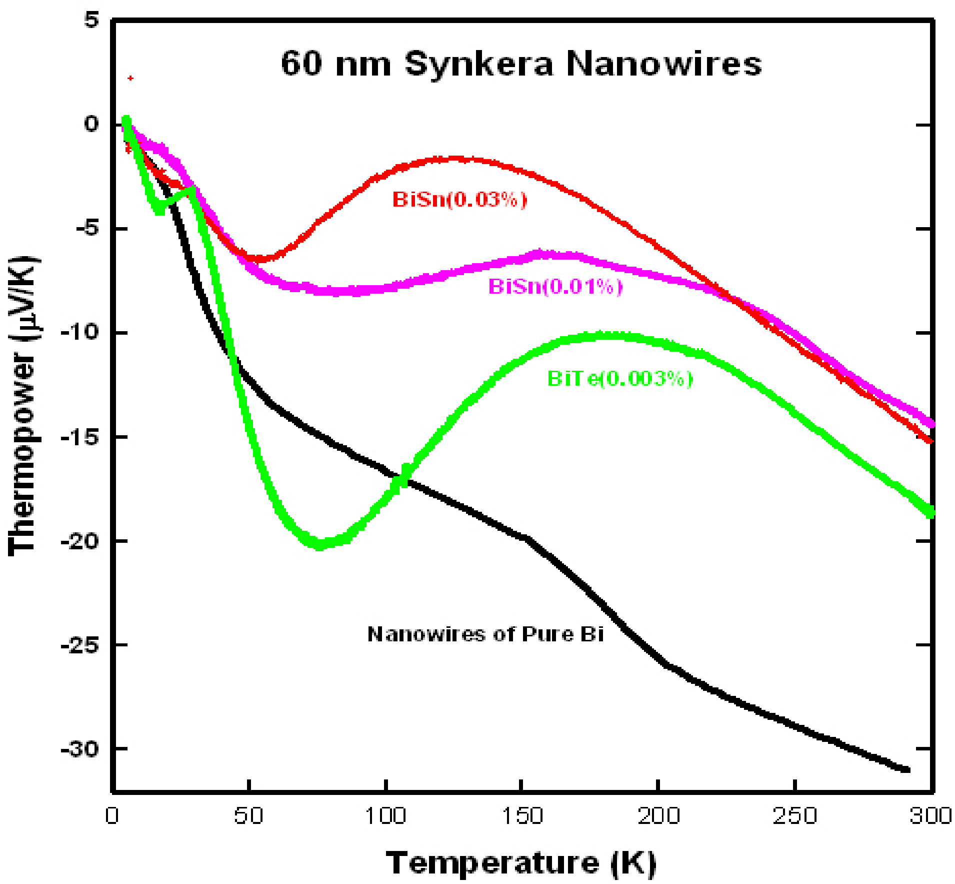


Figure 11. *Thermopower of arrays of 60-nm doped Bi nanowires. These arrays are based on templates made by Synkera Technologies.*

The main result is that since the slope of the thermopower at low temperatures is basically the same for all the alloys. We conclude that **doping does not affect the surface charge** drastically (the changes that occur at intermediate temperatures are related to change of electron and hole mobilities in all likehood). This research will be presented in detail in a future publication.

SECTION VI: <u>PRELIMINARY EXPERIMENTS OF TUNING THE FERMI LEVEL WITH A MAGNETIC FIELD.</u>

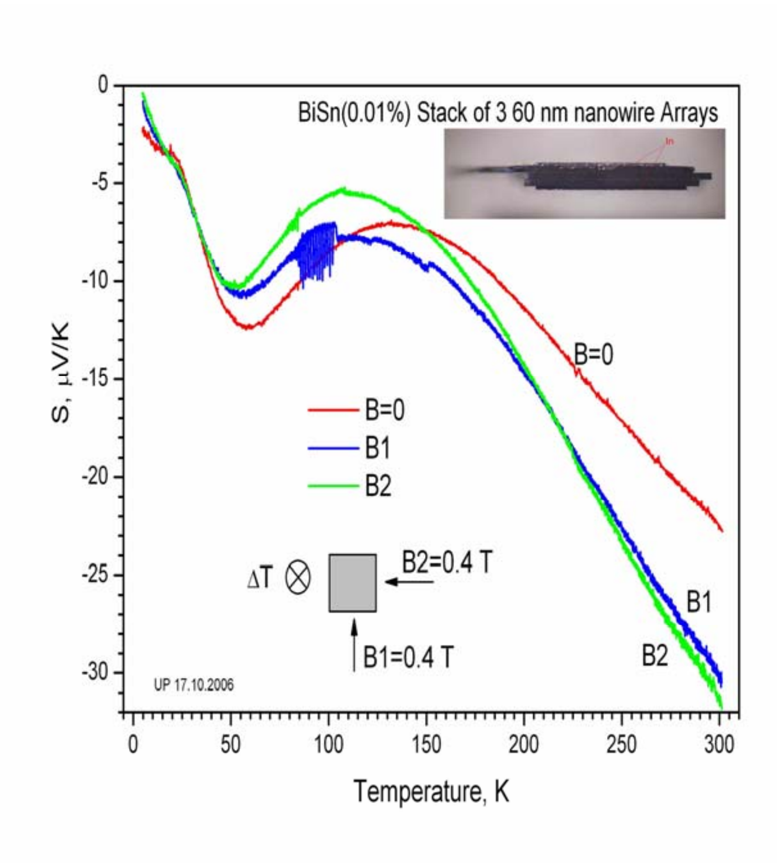


Figure 12. *Transverse magnetic field dependent thermopower of arrays of 60-nm Bi nanowires.*

The thermopower exhibits magnetic field effects at all temperatures, as shown in Figure 12. At high temperature, the effects can be interpreted similarly to the familiar magnetic field effects in the thermopower of bulk Bi; these effects are mobility effects. However, the low temperatures, the observed effects can be considered as evidence that the wavefunction of the surface states remain coherent over the path consisting of a turn around the nanowire. The thermopower effect would arise because, in quantum mechanics, the phase of the surface states wavefunction has an added term (called cyclic phase or Aharonov-Bohm phase). In fact, for a 60-nm nanowire, the magnetic field that changes the phase of the wavefunction by 360^o is 0.8 T when the magnetic field is applied parallel to the wirelength. In this quantum-mechanical scenario, the condition of constructive and destructive interference changes with the magnetic field and therefore the value of the density of surface charge carriers oscillates with applied magnetic field. As is shown by the figure, the thermopower changes by ~ 20% at 50 K with a 0.4 T transverse magnetic field. We were not able to finish this investigation and these results are only preliminary.

There is supporting evidence. We have observed an oscillatory dependence of the low temperature resistance and of the thermopower of individual single-crystal bismuth nanowires on the Aharonov-Bohm phase of the magnetic flux threading the wire. 55 and 75-nm wires were investigated in magnetic fields of up to 14 T. For 55 nm nanowires, longitudinal magnetoresistance periods of 0.8 and 1.6 T that were observed at magnetic fields over 4 T are assigned to *h/2e* to *h/e* magnetic flux modulation. The same modes of oscillation were observed in 75-nm wires. The observed effects are consistent with models of the Bi surface where surface states give rise to a significant population of charge carriers of high effective mass that form a highly conducting tube around the nanowire. An interpretation of the magnetoresistance oscillations in terms of a subband structure in the surface states band due to quantum interference in the tube can be presented. A paper about these results was submitted to the Physical Review in April of 2007. The paper is still under review. The paper is a collaboration with A. Nikolaeva of the Academy of Sciences of Moldova and M. J. Graf of Boston College.

SECTION VII: <u>SUMMARY OF THE MOST IMPORTANT RESULTS.</u>

Gains in the thermoelectric figure of merit have been obtained by decreasing the phonon thermal conductivity of the thermoelectric material. Another approach for better thermoelectrics is the exploitation of electronic quantum confinement effects in nanostructured samples. We have investigated experimentally if quantum confinement effects can lead to a large thermopowers. Previous experimental studies of well characterized samples failed to show an enhancement of the thermopower, but the reason for this failure was not identified. Here we present the results of our research that leads us to conclude that bismuth nanowires have, in addition to bulk electrons and holes, a third type of charge carriers (surface charges). The effect of surface charges is to shift the range of diameters over which the relevant phenomena occurs. We investigated the range of diameters 20-200 nm and report thermopower enhancements in 35 nm Bi nanowire arrays. At room temperature, the thermopower of 35 nm nanowire is found to be 95 μV/K, larger than the thermopower of Bi single crystals at the same temperature. We also show that the thermopower can be further optimized by applying a magnetic field.

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